Polymerizable Derivatives of Long-Chain Alcohols

Preparation and Characterization of Copolymers of Vinylidene Chloride and Alkyl Acrylates

▶Efficiency of plasticization increases with chain length until side chain crystallization starts, but tensile strength decreases with increasing acrylate content

AT THE CONCLUSION of a series of studies on copolymers of vinyl chloride and vinyl esters (*9*), it was decided to investigate the effects of a fat-based internal plasticizer on the physical properties of poly(vinylidene chloride), a material more strongly crystalline than poly(vinyl chloride). Three alkyl acrylates of varying chain lengths were chosen as the comonomers for these experimental copolymers—butyl acrylate (short chain), octyl acrylate (intermediate chain), and octadecyl acrylate (long chain). Copolymers of vinylidene chloride containing varying amounts of each of these alkyl acrylates were prepared for measurement of physical properties, so that the effects of both quantity of the alkyl acrylate and length of the alkyl chain could be evaluated.

Alkyl acrylates were chosen for copolymerization with vinylidene chloride because it was expected that any mixture of these two monomers would yield a copolymer homogeneous in composition. Hence variables that might conceivably affect the physical properties of the copolymers would be reduced. This assumption of compositional homogeneity was based in part on the reported (*1*, *8*) monomer activity ratios of 1 to 1 for the monomer pair, methyl acrylate, and vinylidene chloride, and also on previous work (*12*) on a somewhat analogous system which indicated that altering the length of the alkyl chain has little effect on monomer reactivity ratios.

Reagents

Crude octadecyl acrylate was prepared essentially by the method of Rehberg and Fisher (*10*) and was purified by crystallization. The molten crude reaction product was poured into petroleum ether, boiling point 63° to 70° C. (3 ml. of solvent per gram of ester), hydroquinone and poly(ethyl acrylate) were filtered off, the solvent was evaporated at room temperature, and the process was repeated. In the second treatment, the petroleum ether solution was extracted three times with 25% aqueous sodium carbonate containing 1% sodium hydroxide (1 volume of alkaline wash to 3 volumes of monomer solution), freed from alkali, and dried prior to removal of the solvent. The crude ester was then crystallized once from acetone (3 ml. per gram of monomer) at 0° C. The yield was 76%. Octadecyl acrylate has a melting point of 31.0-2.1° C., n_D^{35} 1.4458 (saponfication no., calculated 172.8; found 169.5). When a sample of the ester containing 0.25 weight % benzoyl peroxide (dissolved at 50° C.) was heated for 3 hours at 70° C. in a nitrogen atmosphere, its refractive index rose from 1.4383 to a constant value of 1.4500.

A commercial, inhibited grade of octyl acrylate, boiling point 227–31° C., considered to be 99% pure on the basis of its saponification number, was used. This was freed from inhibitor (hydroquinone) by extraction with 25% aqueous sodium carbonate containing 1% sodium hydroxide (1 volume of monomer per volume of alkaline wash) until the aqueous layer was no longer colored. The monomer was then washed free from alkali, dried, and stored at −20° C. until used.

A commercial, inhibited grade of butyl acrylate, boiling point 145–8° C., considered to be 99% pure on the basis of its saponification number, was purified by three washes of 5% sodium hydroxide–20% sodium chloride solution (20 parts of wash to 100 parts of monomer), followed by water washes until neutral.

Commercial vinylidene chloride was distilled immediately prior to use, and the fraction boiling at 31.0–2.0° C. was selected.

Poly(vinyl alcohol) (98.5% hydrolyzed, $\overline{M}_n$ 40,000) and finely ground magnesium carbonate, ACS grade, were used as the suspension agents. Reagent grade benzoyl peroxide was used as the initiator.

Polymerization Procedure

The copolymers were prepared in suspension by the recipe of Table I. The containers used were crown-capped 32-ounce bottles (*9*), from which oxygen was excluded by flushing with oxygen-free nitrogen before and after addition of the reagents. At the end of the polymerization period, the copolymers were filtered off, washed with water, treated with 200 ml. of 10% sulfuric acid for 10 to 30 minutes to remove the magnesium carbonate, refiltered, and washed until the filtrate was neutral. The unreacted alkyl acrylate was removed by extracting four to five times with refluxing methanol (5 ml. per gram) for 3 hours per extraction. (A petroleum ether extraction was used in some cases to prevent a slight bloom from developing after molding.) The dried copolymers were analyzed for chlorine, from which the alkyl acrylate content was calculated.

The weight average degrees of polymerization (from light-scattering data) and the intrinsic viscosities were determined for several copolymers so prepared. A copolymer containing 7.5 mole % butyl acrylate had a degree of polymerization of 2924 and an intrinsic viscosity of 0.898; 7.7 mole % octyl acrylate, degree of polymerization 2677, $[\eta]$ 0.638; 12.6 mole % octyl acrylate, degree of polymerization 4892, $[\eta]$ 1.120; 7.5 mole % octadecyl acrylate, degree of polymerization 2190, $[\eta]$ 0.630. No study was made relating conditions of polymerization to molecular weight.

Characterization of Copolymers

Copolymer films were prepared by milling 1 part of lead carbonate and 0.5 part of stearic acid with 100 parts of copolymer. When properly fused, these

Table I. Preparation of Copolymers of Vinylidene Chloride

Monomer mixture, g.	200
Poly(vinyl alcohol) solution (0.5%), ml.	400
Magnesium carbonate, g.	6
Benzoyl peroxide, mole %	0.78[a]
Time, hours	48
Temperature, ° C.	50 ± 3

[a] For copolymers containing octadecyl acrylate, following mole per cent of initiator were used for designated mole per cent range of ester: 0.15 (2.5–5), 0.25 (7.5–15), and 0.50 (20).

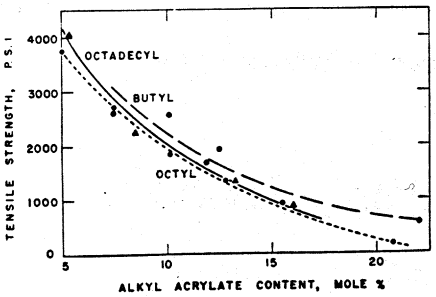

Figure 1. Variation of tensile strength of vinylidene chloride copolymers with mole per cent of alkyl acrylate

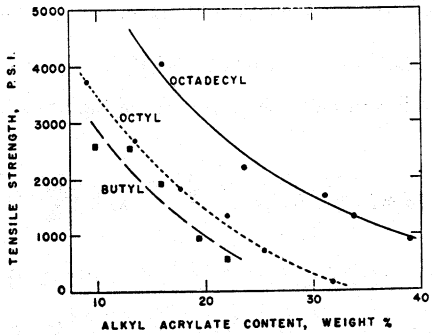

Figure 2. Variation of tensile strength of vinylidene chloride copolymers with weight per cent of alkyl acrylate

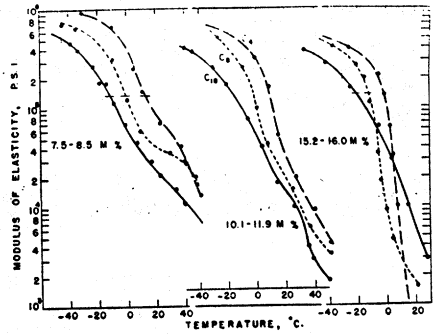

Figure 3. Variation of modulus of elasticity in torsion of several copolymers of vinylidene chloride with temperature

films were molded into 6 × 6 × 0.7 inch sheets, which were used for determination of the physical properties of the copolymers. Mechanical properties (*4*)—i.e., tensile strength, per cent elongation, and 100% modulus—were measured using the Scott I P-4 tensile tester. The torsional modulus was studied as a function of temperature in the apparatus of Clash and Berg (*5*) and of Williamson (*11*).

Electrical properties (the dielectric constant, ϵ', and dielectric loss factor, ϵ'') were determined with a General Radio Co. capacitance measuring assembly containing the following components: Type 716-C capacitance bridge, Type 1302-A oscillator, Type 1474 amplifier and null detector equipped with filter, Type 1603-A and Type 1690 dielectric sample holder. The sample was a disk, 1.75 inches in diameter and 0.05 to 0.07 inch thick, cut from the test sheets previously described. Its temperature, in the range −30° to 120° C., was maintained to ±0.5° by circulating air from a constant temperature bath through the insulated sample holder. Measurements were made at 5° intervals throughout the dispersion range and at 50, 100, 300, 1000, 3000, 10,000, 30,000, and 100,000 cycles per second.

Mechanical Properties

The chief factor determining the tensile properties of the copolymers was the mole per cent alkyl acrylate present; the tensile strength decreased as the alkyl acrylate content increased. This is shown in Figure 1, where the curves for the various copolymers nearly superimpose. On a weight per cent basis (Figure 2), however, the tensile strength decreased less rapidly when the alkyl group was long-chain (see also Table II). The 100% modulus of the copolymers also decreased with increasing alkyl acrylate, while the per cent elongation increased. Viscous flow at the yield point characterized all the copolymers and was especially pronounced in copolymers having a high proportion of an alkyl acrylate. The copolymers were highly resilient—i.e., they recovered their shapes rapidly when released from torsional stress.

The copolymers containing up to 5 mole % octyl or octadecyl acrylate and up to 7.5 mole % butyl acrylate were essentially rigid materials at room temperature. Those containing 7.5 to 12 mole % alkyl acrylate were flexible materials characterized by rapid recovery from distortion at low stresses.

The effect of temperature on the torsional modulus of several copolymers of vinylidene chloride having approximately the same molar proportion of the three alkyl acrylates studied is shown in Figure 3. In general, the modulus at a given temperature decreased with increasing alkyl acrylate content. For a given molar composition at a given temperature, the modulus decreased in the order butyl, octyl, octadecyl, which is similar to the effect noted among copolymers of vinyl chloride and vinyl esters (*9*). As the proportion of alkyl acrylate was increased, the approximate rate of change of modulus with temperature (taken in the modulus interval 10^4 to to 10^5 pounds per square inch) increased, but the effect was least pronounced when the alkyl group was octadecyl.

Table II. Mechanical and Thermal Properties of Copolymers of Vinylidene Chloride and Alkyl Acrylates

Acrylate Content								
Monomer mix., mole %	Copolymer Mole %	Copolymer Wt. %	Yield, %	Tensile Strength, Lb./Sq. Inch	Elongation, %	100% Modulus Lb./Sq. Inch	Milling Temp., ° C.	Clash-Berg T_f, ° C.
Butyl Acrylate Copolymers								
7.5	7.5	9.7	49	2600	45	...	150	12.5
10.0	10.1	12.9	35	2560	90	...	150	8.5
12.5	12.5	15.9	47	1930	200	1860	120	7.0
15.0	15.5	19.5	59	930	400	600	65	2.0
20.0	22.0	27.2	76	590	500	340	55	− 1.5
Octyl Acrylate Copolymers								
5.0	5.0	9.1	79	3750	140	...	155	...
7.5	7.6	13.5	86	2690	280	2660	135	0.0
10.0	10.1	17.6	78	1820	430	1740	110	− 3.5
12.5	12.9	22.0	84	1350	500	1180	65	− 8
15.0	15.2	25.4	88	715	500	550	65	−11.5
20.0	20.8	33.3	89	170	500	110	65	−16
Octadecyl Acrylate Copolymers								
5.0	5.3	15.8	65	4060	110	3950	155	− 7
7.5	8.5	23.7	70	2250	425	2080	145	−11
10.0	11.9	31.1	75	1700	500	1595	120	−16
12.5	13.2	33.7	85	1320	500	1190	70	−18
15.0	16.0	38.9	76	900	430	770	45	−21.5

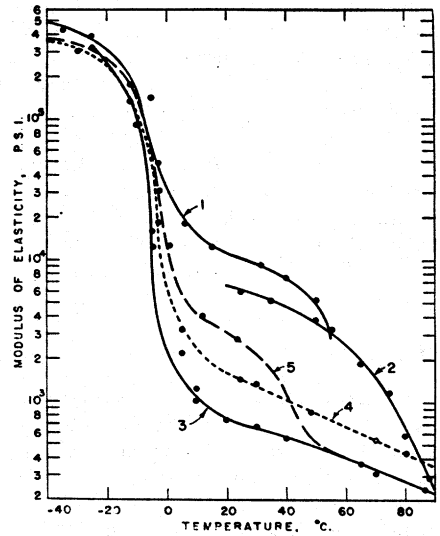

Figure 4. Effect of thermal history on the torsional modulus of a vinylidene chloride copolymer, showing crystallization of copolymer

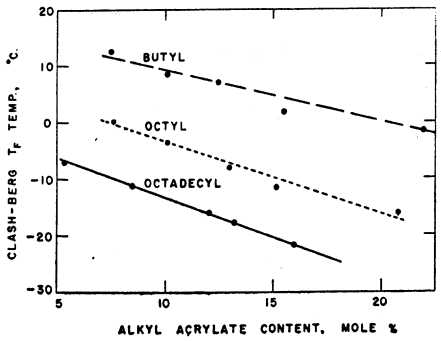

Figure 5. Variation of brittle temperature of several copolymers of vinylidene chloride with mole per cent of alkyl acrylate

Table III. Dielectric Properties of Copolymers of Vinylidene Chloride and Alkyl Acrylates at 30° C.

Frequency, Kc.		Acrylate Ester, Mole %: Butyl, 7.5	Octyl 7.5	Octyl 12.5	Octyl 15.0	Octyl 21.4	Octadecyl 5.5	Octadecyl 8.5	Octadecyl 15.5	Octadecyl 21.2
0.05	ϵ'	4.99	4.57	4.61	4.92	5.12	3.99	3.37	3.82	4.03
	ϵ''	0.1606	0.0516	0.1401	0.0462	0.0394	0.0970	0.0125	0.0390	0.0540
10	ϵ'	3.75	3.73	3.62	3.84	3.95	3.51	3.10	3.53	3.60
	ϵ''	0.1035	0.1167	0.1119	0.1425	0.1659	0.0674	0.0500	0.0628	0.0738
100	ϵ'	3.36	3.19	3.16	3.30	3.25	3.15	2.82	3.16	3.20
	ϵ''	0.0648	0.0868	0.0787	0.0987	0.1112	0.0753	0.0660	0.0799	0.0826

The irregular change of the temperature coefficient of the modulus for some of the copolymers (especially samples C_8 and C_{18} containing 10.1 to 11.9 mole % of the alkyl acrylate) appeared to indicate a transition region at a temperature above 0° C. as well as at lower temperatures. This phenomenon was investigated further and the effects of the thermal history of the sample on the modulus were especially studied. For this work the Williamson (*11*) torsional wire apparatus was used to maintain a high sensitivity in measurement in the low modulus region. In Figure 4, the results of these tests are shown on a copolymer of vinylidene chloride containing 12.7 mole % octyl acrylate. The sample had been conditioned for 2 years before being tested. Curve 1 shows the change in modulus with temperature from −50° to +55° C. The sample was then cooled from 55° to 23° C. and allowed to stand for 24 hours and the moduli were redetermined at the temperatures shown in curve 2. The moduli in the temperature range 23° to 55° are lower than in the previous experiment. Immediately after the conclusion of this experiment, the sample was cooled to −50° C. and the moduli were redetermined at the temperatures shown in curve 3. The plateau which had been present in curves 1 and 2 is now gone and the moduli are much lower. The sample was held at 23° for 24 hours and when the moduli were redetermined from −50 to 90°, curve 4 was obtained. The sample was then again held for 24 hours at 23° C. and the moduli shown in curve 5 were obtained. The progressive increase in modulus and the reappearance of the plateau region will be noted. The reversible time-dependent change in modulus and the presence of the plateau region at a characteristic temperature are strongly suggestive of the occurrence of crystallization and the presence of a first-order transition at about 20° C. A similar but less pronounced phenomenon was observed by Alfrey, Wiederhorn, Stein, and Tobolsky (*2*), who studied plasticized poly(vinyl chloride) by stress relaxation and streaming birefringence.

Thermal Properties

In general, the milling temperature (Table II) decreased as the molar content of the alkyl acrylate increased. The brittle temperature, taken as the Clash and Berg T_f temperature (*5*), also decreased with increasing alkyl acrylate content, as shown in Table II and Figures 5 and 6. The figures show that a long alkyl chain is more effective in decreasing the brittle temperature than a short one.

Dielectric Properties

As is characteristic of other polymeric materials, the dielectric constant of copolymers of vinylidene chloride and alkyl acrylates varied directly with temperature and inversely with frequency. The loss factors likewise passed through a maximum at a temperature characteristic of the copolymer and the frequency of measurement. Selected dielectric data for some copolymers are given in Table III. Both the dielectric constant and the loss factor decrease with the alkyl chain length of the acrylate ester.

Kauzmann (*7*) has shown that dielectric relaxation may be treated as a rate process. Thus it is possible to calculate the free energy, the entropy, and the enthalpy of activation involved in the rotation of a copolymer segment. ΔF was obtained from the familiar rate equation applied to dielectric properties:

$$\frac{1}{\tau} = \frac{kT}{h} e^{-\Delta F^{\neq}_{\epsilon}/RT} \qquad (1)$$

where τ is the relaxation time in seconds (the angular frequency of maximum absorption), k the Boltzmann constant, h the Planck constant, R the gas constant, and T the absolute temperature. Because:

$$\Delta F = \Delta H - T\Delta S \qquad (2)$$

Equation 1 may be written:

$$1/\tau = \frac{kT}{h} e^{\Delta S^{\neq}_{\epsilon}/R} e^{-\Delta H^{\neq}_{\epsilon}/RT} \qquad (3)$$

If log $1/\tau$ is plotted against $1/T$ (Figure 7), $H^{\neq}_{\epsilon}$ is the slope of the line obtained. $\Delta S^{\neq}_{\epsilon}$ is then obtained from Equation 2. If the mole fraction of the modifying comonomer or plasticizer is kept constant and only the nature of the comonomer or plasticizer is changed, the efficiency of plasticization both external and internal may be directly compared from the enthalpy of activation required.

In Figure 8, the change in $\Delta H^{\neq}_{\epsilon}$ with plasticizer content and type is shown. The data for α-chloronaphthalene were taken from the work of Funt and Sutherland (*6*). The enthalpy change required for segment rotation initially decreases as the mole content of external plasticizer (α-chloronaphthalene) or internal plasticizer increases. The plasticization efficiency of α-chloronaphthalene and butyl acrylate are about the same, but octyl and octadecyl acrylate are more efficient in copolymers contain-

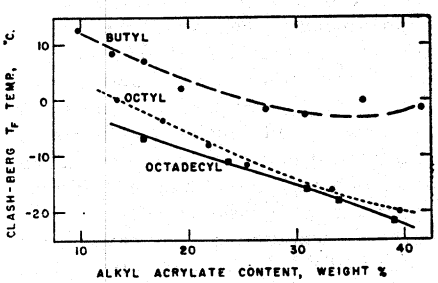

Figure 6. Variation of brittle temperature of several copolymers of vinylidene chloride with weight per cent of alkyl acrylate

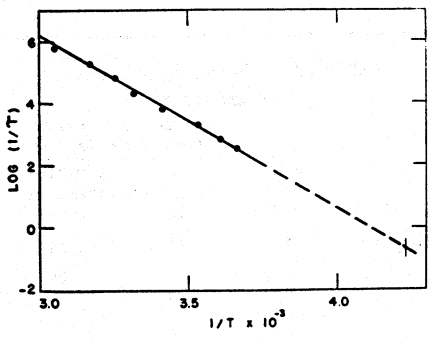

Figure 7. Variation of relaxation time with temperature of a copolymer of vinylidene chloride containing 12.5% octyl acrylate

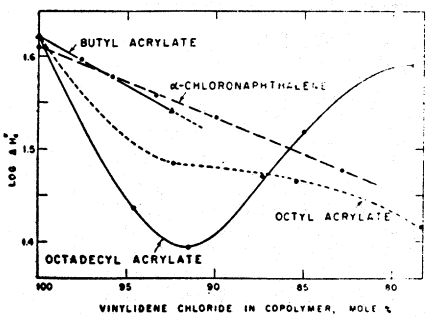

Figure 8. Variation of enthalpy of activation for dielectric relaxation with mole content of plasticizers. Comparison of efficiency of plasticization

ing up to 10 mole % acrylate. The efficiency of octadecyl acrylate passes through a maximum at about 7.5 mole %. This may be due to increasing restriction of segmental motion by increasing side chain association, which culminates in side chain crystallization as the octadecyl acrylate content increases.

If it is assumed that extrapolation of the dielectric data shown in Figure 7 to low frequencies (vertical intersecting line) may be made without serious error, a characteristic low temperature may be calculated in the time scale of the Clash and Berg apparatus, namely, 5 seconds. It is of interest to compare (Table IV) the value of these characteristic temperatures with those obtained using the arbitrarily selected modulus of 1.35×10^5 pounds per square inch which Clash and Berg use as a criterion of brittle temperature. In all cases the characteristic temperature obtained by extrapolation is significantly lower than the brittle temperature. Because these characteristic temperatures are based on thermodynamic considerations it is likely that they correspond to the second-order transition temperature. When these characteristic temperatures are located on the torsional modulus curves of Figure 3 (vertical intersecting lines), they appear at approximately the point of the curve where the rate of change of curvature is at a maximum. The corresponding T_f temperatures appear at the intersection with the horizontal lines.

Table IV. Characteristic Low Temperatures

Copolymer	Mole % Acrylate	Characteristic Low Temperatures, °C. Clash-Berg T_f	Dielectric extrapolation
Butyl	7.5	12.5	−14
Octyl	7.7	0	−28
	12.7	− 8	−28
	14.6	−11	−26
	21.7	−15	−36
Octadecyl	5.3	− 7	−44
	8.5	−11	−46
	15.9	−21.5	−31
	21.2		−22

Table V. Tensile and Thermal Properties of Oriented and Unoriented Vinylidene Chloride Copolymers

Acrylate	Mole %	Tensile Strength, Lb./Sq. Inch	Elongation, %	Clash-Berg T_f, °C.
Butyl	10.1			
Unoriented		2560	90	
Oriented		12,000	80	
Octyl	10.1			
Unoriented		1820	430	− 3.5
Oriented		9050	75	− 8
Octadecyl	5.8			
Unoriented		2910		
Oriented		9870		
Octadecyl	11.9			
Unoriented		1700	7500	−16
Oriented		6750	70	−19

Solubility and Resistance to Reagents

Although poly(vinylidene chloride) is insoluble in most organic solvents, the copolymers of vinylidene chloride and alkyl acrylates showed increasing solubility as the alkyl acrylate content was increased from 2.5 to 15 mole %. Common chlorinated solvents such as chlorobenzene, chloroform, and ethylene chloride and other solvents such as benzene and tetrahydrofuran were found to be solvents for the copolymers containing 10 to 15 mole % of the alkyl acrylate. Copolymers containing butyl acrylate were more soluble than those containing the longer-chain acrylates.

The resistance of several of these copolymers to selected reagents was tested by an ASTM procedure (*3*). Copolymers containing up to approximately 10 mole % of butyl acrylate and 5 mole % of octyl acrylate were unaffected by 10% sodium hydroxide solution, cottonseed oil, kerosine, or 3 or 30% sulfuric acid (change in weight after 7 days 1% or less). Copolymers containing 10% octyl acrylate or up to 10% octadecyl acrylate were unaffected by the alkali or acid but absorbed significant amounts of cottonseed oil and kerosine. The weight of reagent absorbed varied with acrylate content.

Effect of Orientation on Samples

To determine the effect of orientation on these copolymers, 1 × 1 inch sheets of the films were stretched at room temperature until their length increased to approximately 4 inches and their thickness was decreased from 0.07 to 0.03 inch. The tensile strength and elongation of the oriented films were measured by using the Plastiversal tensile tester, and their torsional modulus was studied as a function of temperature by using the apparatus of Clash and Berg. The effect of orientation on these properties is shown in Table V. A greater increase in tensile strength (both in actual value and on a percentage basis) was produced with a short-chain than with a long-chain alkyl acrylate. Brittle temperature decreased slightly.

Orientation did not improve the resistance of the copolymer films to the selected reagents mentioned above; in fact, a copolymer containing 10 mole % of octadecyl acrylate increased in weight almost twice as much as the corresponding unoriented material and showed much greater dimensional change when immersed in these reagents.

Acknowledgment

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